ACCESSION NR: AP4040487

Elementoorganic Compounds, AN SSSR)

SUBMITTED: 11Jul63 DATE ACQ: 06Jul64 ENCL: 00

SUB CODE: GC NO REF SOV: 003 OTHER: 008

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ACCESSION NR: AP4040488 S/0190/64/006/006/1087/1091

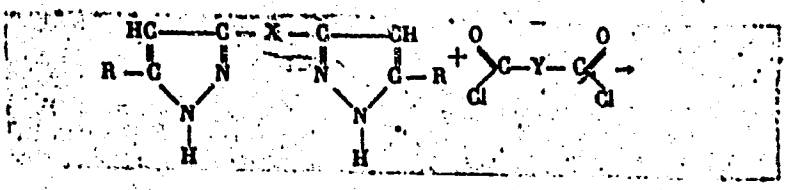
AUTHORS: Korshak, V. V.; Krongauz, Ye. S.; Berlin, A. M.; Travnikova, A. P.

TITLE: Synthesis of polymers by the polycyclization reaction. 6. Polypyrazoles

SOURCE: Vysokomolekulyarnyye soyedineniya, v. 6, no. 6, 1964, 1087-1091

TOPIC TAGS: polycyclization reaction, polypryazole, bipyrazole polycondensation, dicarboxylic acid chloride, diketone polycyclization, dicarboxylic acid dihydrazide

ABSTRACT: The investigators attempted to synthesize polypyrazoles from compounds containing pyrazole cycles. The desired results were achieved by polycondensation of bipyrazoles with the chlorides of dicarboxylic acids according to the reaction



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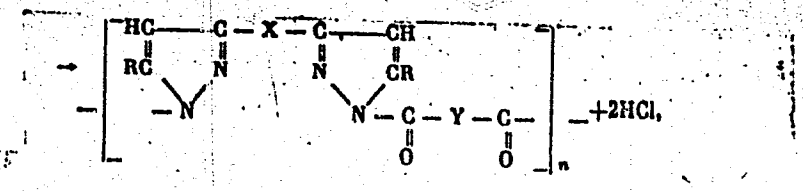
ACCESSION NR: AP4040466



where X = $C_6H_4(CH_2)_2C_6H_4$; $C_6H_4OC_6H_4$; $CH_2C_6H_4CH_2$; $(CH_2)_8$; R = CH_3, C_6H_5; Y = $(CH_2)_4$, C_6H_4.

A total of 8 bypyrazoles were synthesized. Seven of them were new and represented: 4,4'-bis-(5-methylpyrazolyl-3)diphenyloxide, 4,4'-bis-(3,5-dimethylpyrazolyl-4) xylilene, 4,4'-bis-[(3,5-dimethylpyrazolyl-4)methyl]diphenyloxide, 4,4'-bis-[(3,5-dimethylpyrazolyl-4)methyl]diphenyl, 1,8 di-(5-phenyl-pyrazolyl-3)octane, di-(3,5-dimethylpyrazolyl-4), and 4,4'-bis-(5-methylpyrazolyl-3)diphenyldisulfide. The procedure was started by mixing 30-40 ml of pyridine with 0.1 mole quantities of one of the bypyrazoles. To these mixtures were added (dropwise) 0.1 mole amounts of adipic, terephthalic, or isophthalic acid chloride, dissolved in 20 ml of xylene. The contents of the flasks were stirred and cooled for several hours. They were then heated for a long time to 100-125C, and were allowed to stand overnight. The polypyrazoles so produced were identical with the polypyrazoles ob-

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tained by polycyclization of bis-(β-diketones) with the dihydrazides of the corresponding dicarboxylic acids. The latter group was described in an earlier publication by the authors and P. N. Gritkova (Dokl. AN SSSR, 148, 602, 1963). Orig. art. has: 3 tables and 1 formula.

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SUBMITTED: 11Jul63 DATE ACQ: 06Jul64 ENCL: 00

SUB CODE: GC NO REF SOV: 004 OTHER: 006

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ACCESSION NR: AP4042185 S/0190/64/006/007/1195/1202

AUTHOR: Korshak, V. V.; Krongauz, Ye. S.; Berlin, A. M.; Smirnova, T. Ya.

TITLE: Synthesis of polymers by polycyclization. Polypyrazoles. VII.

SOURCE: Vy*sokomolekulyarny*ye soyedineniya, v. 6, no. 7, 1964, 1195-1202

TOPIC TAGS: polypyrazole, polycyclization reaction, bis-(β-diketone), dihydrazine, hexamethylenehydrazine dihydrochloride, p-phenylene-hydrazine dihydrochloride, polypyrazole property

ABSTRACT: The authors have synthesized polypyrazoles (mp,. 200—300C) by polycylization of linear and branched bis-(β-diketones) with dihydrazides of dicarboxylic acids. In an attempt to develop polypyrazoles with a higher heat resistance, dihydrazides were replaced with dihydrazine, or amide groups were introduced in the polymers to form hydrogen bonds. Polycyclization of bis-(β-diketones) with hexamethylene- or p-phenylenehydrazine dihydrochlorides in boiling alcohol with alkali added to separate and bind HCl, or heating equimolar amounts of the initial materials in pyridine, yielded

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polypyrazoles — powders with a mp of 80—265C and a molecular weight of 5000. Polypyrazoles containing amide groups in the backbone were synthesized by reacting dipyrazoles with diisocyanates in chlorobenzene or by melting the initial materials in nitrogen. These polymers are white powders with a mp of 208—276C and a molecular weight of up to 10,000. IR spectra indicate that they do not contain hydrogen bonds. Thus, the attempt to synthesize heat-resistant polypyrazoles failed. The presence of heavy pyrazole rings upsets the symmetry and loosens the packing density of the polymer chains, and, as a result, prevents the formation of hydrogen bonds. Orig. art. has: 1 figure and 2 tables.

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SUBMITTED: 11Jul63 ATD PRESS: 3068 ENCL: 00

SUB CODE: OC, GC NO REF SOV: 009 OTHER: 003

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